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(54) **Rubber composition with improved wet skid and heat build-up properties**

(57) A rubber composition comprising (A) from 10 to 90% by weight of a random styrene-butadiene copolymer having a bound styrene content of from 3 to 30% by weight and a butadiene portion which has a 1,2 content of from 60 to 95% by weight, said copolymer being obtained by

polymerization in the presence of an organoalkali metal catalyst and (B) from 90 to 10% by weight of at least one rubber having a glass transition temperature not higher than -40°C , said rubber being natural rubber, polyisoprene rubber, styrene-butadiene copolymer rubber or polybutadiene rubber, has improved wet skid and heat build-up properties and is useful as a rubber for automobile tyre treads.

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SPECIFICATION

Rubber composition

This invention relates to a novel rubber composition particularly suitable for use as a tyre tread.

When considering the performance of rubber for use as an automobile tyre tread, particular importance has recently been attached to good wet skid properties (which are concerned with running stability), as well as to good heat build-up properties, high durability and low rolling friction resistance (which affect fuel consumption). 5

No single rubber capable of possessing all of these properties is known and, as a result, blends of different kinds of rubber have been used for the purpose of harmonizing these properties. For example, a composition composed of a styrene-butadiene copolymer rubber and a polybutadiene rubber has been widely used as the tread rubber for passenger cars. However, this composition does not always exhibit satisfactory wet skid properties. One way of improving wet skid properties is to incorporate a resin having a high glass transition temperature into the composition. However, this can cause deterioration of dynamic characteristics, particularly heat build-up properties, and is consequently an unsatisfactory solution. 10 15

We have now discovered a novel rubber composition having improved wet skid and heat build-up properties.

According to this invention, there is provided a rubber composition comprising: (A) from 10 to 90% by weight of a random styrene-butadiene copolymer having a bound styrene content of from 3 to 30% by weight and a butadiene portion which has a 1, 2 content of from 60 to 95% by weight, said copolymer being obtained by polymerization in the presence of an organo-alkali metal catalyst; and (B) from 90 to 10% by weight of at least one rubber having a glass transition temperature not higher than -40°C , said rubber being natural rubber, polyisoprene rubber, styrene-butadiene copolymer rubber or polybutadiene rubber. 20

The term "random styrene-butadiene copolymer" as used herein means a styrene-butadiene copolymer, the bound styrene of which contains 10% by weight or less of block styrene, measured according to the oxidative decomposition method described by I. M. Kolthoff *et al.*, J. Polymer Sci., 1, 429 (1946). 25

Although the rubber composition of this invention has substantially identical heat build-up properties to conventional tyre tread rubber compositions, it has markedly improved wet skid properties. Further, its heat build-up properties are much better than those of rubber compositions, the wet skid properties of which have been improved by adding a polymer having a high glass transition temperature (such as resins, high-styrene rubber or the like). Further, it also has excellent compatibility between the blended rubbers and good processability. These characteristics of the composition are achieved by using, as a part of the rubber component, a random styrene-butadiene copolymer having a bound styrene content of from 3 to 30% by weight (preferably from 5 to 20% by weight) and having a butadiene portion which has a 1, 2 content of from 60 to 95% by weight (preferably from 70 to 95% by weight, more preferably from 80 to 95% by weight). The copolymer (A) also preferably has a Mooney viscosity ($\text{ML}_{1+4}^{100^{\circ}\text{C}}$) of from 20 to 150. The copolymer is obtained by polymerization in the presence of an organo-alkali metal catalyst. 30 35 40

If the bound styrene content of the copolymer (A) is less than 3% by weight, the tensile strength of the rubber composition is too low. On the other hand, if the bound styrene content exceeds 30% by weight, the heat build-up properties of the rubber composition deteriorate. If the 1, 2 content in the butadiene portion is less than 60% by weight, the wet skid properties of the rubber composition deteriorate. A Mooney viscosity of less than 20 is undesirable in respect of tensile strength and heat build-up properties, and a Mooney viscosity exceeding 150 is undesirable in respect of processability. 45

The organo-alkali metal catalysts used to prepare the copolymers (A) are preferably organolithium, organosodium or organopotassium compounds, of which organolithium compounds are particularly preferable. The random styrene-butadiene copolymer (A) can be prepared, for example, by polymerizing styrene and butadiene in a hydrocarbon solvent in the presence of an additive such as an ether or a tertiary amine and using an organolithium compound as initiator, as mentioned in, for example Japanese Patent Publication No. 15,386/61 and No. 41,038/73. The styrene-butadiene copolymer (A) used in the composition of this invention can also be obtained by the process mentioned in, for example, Japanese Patent Application Kokai (i.e. as laid open to public inspection No. 101,287/77. 50

In the composition of this invention, the random styrene-butadiene copolymer (A) is used in a proportion of from 10 to 90% by weight, preferably from 20 to 80% by weight. If this proportion is less than 10% by weight, the wet skid properties are not improved; on the other hand, if it is higher than 90% by weight, the failure properties become bad, and this is undesirable. 55

The rubber (B) with which the random styrene-butadiene copolymer (A) is to be blended is a diene rubber having a glass transition temperature (T_g) not higher than -40°C and preferably not higher than -50°C . Suitable such rubbers include: natural rubber; a high *cis*-1,4-polyisoprene rubber obtained by 60

organolithium catalyst; a high *cis*-1,4-polybutadiene obtained by polymerization with a Ziegler catalyst; and a low *cis*-polybutadiene obtained by polymerization with an organolithium catalyst. By using a rubber having a T_g not higher than -40°C , a rubber composition having excellent abrasion resistance and durability can be obtained. On the other hand, if a rubber having a higher T_g is used, the temperature due to heat build-up becomes undesirably high although the wet skid resistance is improved. A single one of these natural or synthetic rubbers may be used or a combination of two or more of them may be used, in an overall proportion of from 10 to 90% by weight, based on the weight of the composition.

In practice, the rubber composition of this invention is compounded with a process oil, carbon black, a filler, an antioxidant, an antiozonant, zinc oxide, stearic acid, a vulcanization accelerator, a vulcanizing agent and the like, as is well known in the art.

Vulcanizates of the rubber composition of this invention have excellent wet skid properties and low heat build-up, so that they are suitable for use as tyres, including use as a tread rubber.

Furthermore, in addition to their use as tyres, the rubber composition of this invention can be used as industrial rubbers, making the best of its characteristic features, for example, as an industrial belt having good heat resistance and traction.

This invention is illustrated by the following Examples.

Examples 1—4 and Comparative Examples 1—3

Styrene and 1,3-butadiene were added as monomers to a 8 litres of cyclohexane and polymerized using potassium dodecylbenzenesulphonate and diethylene glycol dimethyl ether, respectively, as a randomizing agent and as a 1,2-content regulator for the butadiene part, and using *n*-butyllithium as a polymerization initiator. 2,6-Di-*t*-butyl-*p*-cresol was added to the resulting polymer solution in an amount of 1.0 part by weight per 100 parts by weight of solution, after which the solvent was removed by steam stripping and the residue was dried at 100°C on a roll to obtain a polymer. The conditions for the polymerization and the main properties of the polymer obtained are shown in Tables 1 and 2, respectively. The styrene-butadiene copolymer or polybutadiene thus obtained was then blended with natural rubber and compounding agents by means of a Banbury mixer and rolls, using the compounding recipe shown in Table 3, and was then vulcanized at 145°C for 45 minutes.

The physical properties of the vulcanizates obtained are shown in Table 4.

The compositions of Examples 1—4 have a high tensile strength, a high elongation, a high wet skid resistance and a low temperature due to heat build-up. The composition of Comparative Example 1 is inferior in tensile strength and elongation. The composition of Comparative Example 2 is inferior in wet skid resistance. The composition of Comparative Example 3 is inferior in heat build-up characteristic.

TABLE 1

Ex. or Comp. Ex. No.	Amount (g) of				Polymerization		Polymer yield (%)
	1,3-butadiene	styrene	n-BuLi	KDBS	DGDE	temperature (°C)	time (hours)
1	870	130	0.50	0	1.05	40	1.5
2	930	70	0.55	0.31	1.15	45	1.0
3	820	180	0.45	0.25	0.85	50	1.0
4	750	250	0.42	0	0.61	45	1.5
Comp 1	1000	0	0.58	0.33	1.20	40	1.5
Comp 2	750	250	0.43	0.24	0.10	55	2.0
Comp 3	680	320	0.39	0.22	0.82	40	1.5

Notes:

n-BuLi = n-butyllithium

KDBS = potassium dodecylbenzenesulphonate

DGDE = diethylene glycol dimethyl ether

TABLE 2

Ex. or Comp. Ex. No.	Bound styrene (wt.%)	Block styrene (wt.%)	Butadiene portion microstructure (%)			Mooney viscosity ML ₁₊₄ ^{100°C}
			<i>cis</i> -1,4	<i>trans</i> -1,4	1,2	
1	13	0	7	8	85	47
2	7	0	8	12	80	46
3	18	0	10	19	71	45
4	25	2	16	22	62	45
Comp 1	0	0	6	9	85	48
Comp 2	25	0	28	42	30	47
Comp 3	32	0	6	9	84	45

TABLE 3

	Parts by weight
Styrene-butadiene copolymer or polybutadiene	50
Natural rubber (RSS 1) ⁴⁾	50
ISAF type carbon	50
Aromatic process oil ³⁾	10
Zinc oxide	4
Stearic acid	2
Accelerator MSA ¹⁾	0.54
Accelerator DM ²⁾	0.335
Sulphur	2.0

Notes:

¹⁾ *N*-Oxydiethylene-2-benzothiazylsulphenamide²⁾ Dibenzothiazyl disulphide³⁾ high-aromatic process oil manufactured by Japan Synthetic Rubber Co., Ltd.⁴⁾ Tg: -77°C, as measured with a differential scanning calorimeter at a temperature-raising speed of 20°C/minute.

TABLE 4

Ex. or Comp. Ex. No.	300% Modulus (kg/cm ²) ¹⁾	Tensile Strength (kg/cm ²) ¹⁾	Elongation (%) ¹⁾	Hardness (JIS-A) ¹⁾	Wet skid resistance ²⁾	Heat build-up temp (°C) ³⁾
1	104	240	580	67	75	17
2	103	237	580	65	74	17
3	101	250	620	66	74	18
4	103	260	630	66	73	20
Comp 1	104	200	480	65	75	18
Comp 2	98	260	600	66	67	21
Comp 3	103	230	480	66	75	23

Notes:

- ¹⁾ Measured according to JIS (Japanese Industrial Standard) K-6301.
²⁾ Measured on an indoor asphalt road at 25°C with a skid tester manufactured by Stanley Co. (G.B.).
³⁾ Goodrich heat build-up, measured according to ASTM D 623/58 (Method A).

Examples 5—7 and Comparative Examples 4—5

Using the random styrene-butadiene copolymers of Example 1, vulcanizates were prepared by varying the blend ratio of the copolymers to *cis*-1,4-polybutadiene, and the physical properties of the vulcanizates were evaluated. The compounding recipe and the conditions for vulcanization are shown in Table 5, and the physical properties of the vulcanizates are shown in Table 6.

The compositions of Examples 5—7 have high wet skid resistance, have excellent modulus, tensile strength, tear strength and flex cracking propagation resistance, and are well balanced in these properties.

TABLE 5

	Comparative Example 4	Example 5	Example 6	Example 7	Comparative Example 5
Styrene-butadiene copolymer of Example 1. (parts by weight)	5	25	50	75	95
<i>Cis</i> -1,4-polybutadiene ¹⁾ (parts by weight)	95	75	50	25	5
ISAF type carbon (parts by weight)	50	50	50	50	50
Aromatic process oil (parts by weight)	10	10	10	10	10
zinc oxide (parts by weight)	3	3	3	3	3
Stearic acid (parts by weight)	1.5	1.5	1.5	1.5	1.5
Accelerator DPG ²⁾ (parts by weight)	0.35	0.35	0.35	0.35	0.35
Accelerator DM ³⁾ (parts by weight)	0.90	0.90	0.90	0.90	0.90
Sulphur (parts by weight)	1.6	1.6	1.6	1.6	1.6
Conditions for vulcanization	145°C, 15 min.				

Note:

¹⁾ BRO1, manufactured by Japan Synthetic Rubber Co., Ltd. Mooney viscosity ($ML_{1+4}^{100^\circ\text{C}}$): 45,

T_g: -120°C, *cis*-1,4: 95%, *trans*-1,4: 3%, 1,2: 2%)

²⁾ Diphenylguanidine

³⁾ Dibenzothiazylsulphide

TABLE 6

Ex. or Comp. Ex. No.	300% Modulus (kg.f/cm ²) ¹⁾	Tensile strength (kg.f/cm ²) ¹⁾	Elongation (%) ¹⁾	Hardness (JIS-A) ¹⁾	Tear strength (kg.f/cm ²) ¹⁾	Crack propagation resistance ²⁾	Wet skid resistance	Heat build-up temp/ΔT(°C)
Comp 4	73	210	660	61	42	100	39	21
5	79	200	630	62	40	98	55	21
6	81	195	590	63	39	95	59	21
7	82	195	580	63	38	90	60	21
Comp 5	82	180	540	63	36	70	60	21

Note:

1) Measured according to JIS 6301.

2) With De Mattia testing machine (300 cycles/min.), the number of repetitions of flexing until the initial cut of 2mm propagated to 15mm was measured, and indicated by an index, taking the result in Comparative Example 4 as 100 (a greater value of the index means higher resistance to flex cracking propagation).

CLAIMS

1. A rubber composition comprising:
- 5 (A) from 10 to 90% by weight of a random styrene-butadiene copolymer having a bound styrene content of from 3 to 30% by weight and a butadiene portion which has a 1, 2 content of from 60 to 95% by weight, said copolymer being obtained by polymerization in the presence of an organo-alkali metal catalyst; and 5
- (B) from 90 to 10% by weight of at least one rubber having a glass transition temperature not higher than -40°C , said rubber being natural rubber, polyisoprene rubber, styrene-butadiene copolymer rubber or polybutadiene rubber. 10
2. A rubber composition according to Claim 1, wherein the random styrene-butadiene copolymer (A) has a bound styrene content of from 5 to from 20% by weight and the butadiene portion has a 1, 2 content of from 70 to 95% by weight. 10
3. A rubber composition according to Claim 1 or Claim 2, wherein the random styrene-butadiene copolymer (A) has a Mooney viscosity of from 20 to 150.
- 15 4. A rubber composition according to any preceding Claim, wherein said organo-alkali metal catalyst is an organolithium, organosodium or organopotassium compound. 15
5. A rubber composition according to any preceding Claim, wherein the amount of the random styrene-butadiene copolymer (A) is from 20 to 80% by weight.
6. A rubber composition according to any preceding Claim, wherein said rubber (B) has a glass 20 transition temperature not higher than -50°C . 20
7. A rubber composition according to Claim 1, substantially as hereinbefore described with reference to any one of the foregoing Examples.
8. A vulcanized rubber composition, wherein the rubber component is a rubber composition according to any preceding Claim.

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